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Characterization of Emissions from a Methanol Fueled Motor Vehicle

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16. ABSTRACT

Exhaust, evaporative, and refueling emissions were examined from a methanol fueled Ford Escort operated with M-85 (85% methanol - 15% gasoline) and M-100 (100% methanol) fuels. Exhaust and evaporative emissions were examined for vehicle operation at summer and winter ambient temperatures, while refueling emissions were examined at typical summer temperatures. Regulated emissions (total hydrocarbons, carbon monoxide, nitrogen oxides), as well as, formaldehyde, methanol, and detailed hydrocarbon emissions were examined. Results indicated that carbon monoxide, methanol, hydrocarbon, and formaldehyde exhaust emissions increased substantially when the vehicle was operated at reduced temperatures. Formaldehyde emissions were more fuel sensitive than hydrocarbon, carbon monoxide and methanol emissions. With M-85 a significant portion of the total organic evaporative and refueling emissions was comprised of hydrocarbons. Both hydrocarbon and methanol evaporative emissions were dependent on test temperature as well as on fuel type. Methanol refueling emissions were invariant to both tank temperature and fuel type, while hydrocarbon refueling emissions decreased with increasing tank temperature.

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Characterization of Emissions from a Methanol Fueled Motor Vehicle

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Exhaust, evaporative, and refueling emissions were examined from a methanol fueled Ford Escort operated with M85 (85 percent methanol-15 percent gasoline) and M100 (100 percent methanol) fuels. Exhaust and evaporative emissions were examined for vehicle operation at summer and winter ambient temperatures, while refueling emissions were examined at typical summer temperatures. Regulated emissions (total hydrocarbons, carbon monoxide, nitrogen oxides) as well as formaldehyde, methanol, and detailed hydrocarbon emissions were examined. Results indicated that carbon monoxide, methanol, hydrocarbon, and formaldehyde exhaust emissions increased substantially when the vehicle was operated at reduced temperatures. Formaldehyde emissions were more fuel sensitive than hydrocarbon, carbon monoxide and methanol emissions. A significant portion of the total organic evaporative and refueling emissions with M85 fuel was comprised of hydrocarbons. Both hydrocarbon and methanol evaporative emissions were dependent on test temperature as well as on fuel type. Methanol refueling emissions were invariant to both tank temperature and fuel type, while hydrocarbon refueling emissions decreased with increasing tank temperature.

Interest in methanol as an alternate fuel for motor vehicles has steadily increased over the last decade. As a fuel for high compression engines, the energy efficiency is as good as or better than that observed with gasoline and diesel fuels. Technology is available to produce methanol economically from the abundant reserves of natural gas and coal found in the United States. Indicative of the interest in methanol fuel, prototype methanol fueled vehicles have been developed by the major automobile manufacturers, and EPA has issued proposed rulemaking for regulation of emissions from these motor vehicles.[1] Test fleets of limited-production methanol fueled vehicles are being operated in several parts of the United States and around the world.

Associated with an increase in methanol fuel usage in automobiles, is the potential for increased levels of formaldehyde and methanol in the atmosphere. Previous studies have shown that both of these compounds are elevated in emissions from motor vehicles fueled with methanol and methanol/gasoline blends.[2] Because of the photochemical reactivity of formaldehyde and the health risks associated with exposure to formaldehyde and methanol, research is actively being conducted to quantify these emissions from methanol fueled vehicles.

Previous studies have focused primarily on emissions obtained under certification conditions. In this study, emissions from an "in-use" methanol fueled vehicle operated under noncertification conditions were examined. Exhaust emissions data were obtained for a vehicle operated at a low ambient temperature (40° and 20° F) on EPA's urban dynamometer driving schedule (UDDS) and on a modified version of this cycle which included a five-minute preliminary warm-up idle. Diurnal and hot soak evaporative emissions were also determined at these reduced temperatures. Finally, refueling emissions were determined using fuel temperatures typical of summertime conditions. Emissions examined include total hydrocarbons (THC), carbon monoxide (CO), oxides of nitrogens (NOx), methanol (MeOH), aldehydes, and detailed hydrocarbons (HC).

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Experimental Procedures

Vehicle and Test Fuel Description

The test vehicle used in this study was a 1983 Ford Escort equipped with a 1.6 liter methanol fueled engine, designed to be operated on an 85%/15% (vol./vol.) mixture of MeOH and gasoline. The methanol fueled engine was available from Ford as part of an option package for the 1983 model year Escort. Its basic design is the same as for the 1.6 liter gasoline engine, the biggest difference being an increased compression ratio, from 8.8:1 to 11.8:1. As part of the MeOH option package, the standard base carburetor was modified for operation on MeOH fuel; a supplementary electric fuel pump was added to reduce vapor lock during hot restart; spark plugs two heat ranges colder were used to prevent pre-ignition; ignition timing was adjusted for operation on MeOH fuel; and lastly, fuel system components were constructed from materials resistant to the corrosive properties of MeOH. Emission control devices, which include a three way air injected catalyst, were identical to those found on gasoline powered Escorts.

The vehicle was obtained by EPA from the City of Baltimore, where it had accumulated 16,000 miles in the city's vehicle fleet. Upon delivery, electrical wiring and vacuum hoses were checked for proper routing and the ignition timing was checked and found to be within manufacturer's specifications; therefore, no adjustments were made to the vehicle prior to testing.

Three different MeOH test fuels were used in this study: two MeOH/gasoline blends and pure MeOH (M100). The first blend, M85sg, consisted of MeOH blended with an unleaded summer grade gasoline. The second blend, M85wg, was blended for higher Reid vapor pressure (RVP) using an unleaded winter grade gasoline to improve vehicle cold start properties

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Table I. Description of test fuels.

Property	Test fuels M85sg	M85wg	M100	Blending stock "summer" gasoline	"winter" gasoline
% Methanol	82.0	83.0	100	0	0
Reid-Vapor pressure, psig	8.5	8.8	4.6	11.2	14.9
% Aromatics				37.6	44.8
% Paraffins				52.2	43.6
% Olefins				10.2	11.6
% Distilled @					
65°C				21	26
77°C				31	34
118°C				61	71
190°C				96	94
End point,°C				215	216
% Recovered				97	97
% Residue				1.0	1.0
Octane Index, $\frac{M+R}{2}$				92.3	89.4
Pb, g/gal				0.005	0.032

at reduced ambient temperatures. RVP and percent MeOH for the three test fuels, as well as specifications for the summer and winter grade blending stock are given in Table I. MeOH was purchased in 55 gallon drums from McKesson Chemical Company. Fuel blends were prepared by adding appropriate volumes of either the summer grade or winter grade gasoline to each MeOH drum. Each blend was then analyzed for RVP and % MeOH.

Exhaust and evaporative tests were conducted using each fuel at two different temperatures: 70 and 40°F for the M85sg fuel, 40 and 20°F for the M85wg fuel. Because of vehicle driveability problems encountered with the M100 test fuel at reduced temperatures, the M100 test fuel was used at 70°F only. Refueling tests were conducted with the M85sg and M100 test fuels only.

Exhaust Emissions Determination

Vehicle exhaust emission tests were conducted with an electric chassis dynamometer (Horiba Instruments, Inc.) to simulate vehicle road load. The dynamometer rolls were enclosed within a 370 square foot temperature controlled test chamber (TCTC) permitting vehicle soak and operation at temperatures of 20±4 to 75±4°F. Figure 1 shows an overhead view of the test facilities. Exhaust gases were sampled using the constant volume sampling (CVS) techniques commonly used for vehicle certification tests. A heated transfer tube was used within the TCTC to direct vehicle raw exhaust to the dilution tunnel. Exhaust gas was thoroughly mixed in the dilution tunnel with 70°F diluent air. Total flow through the dilution tunnel was held constant (600 CFM) using the CVS. Samples of diluted exhaust were collected directly from the dilution tunnel at a constant flowrate over the duration of the test, permitting pollutant mass emission rates to be determined from sample concentration and totalized flows. The sampling system had been previously qualified for quantitative transfer of formaldehyde at low temperature.[3]

Samples for MeOH analysis were collected from the dilution tunnel at a sampling rate of 4 L/min using two water filled impingers connected in series. Each impinger contained 25 ml water. MeOH samples were subsequently analyzed by gas chromatography.[4]

Aldehyde samples were collected from the dilution tunnel through a heated (110°C) sample line at a sampling rate of 1 L/min. Aldehyde samples were collected on dinitrophenyl hydrazine (DNPH)-coated silica gel cartridges. Individual aldehydes, which are trapped on the cartridge as DNPH aldehyde derivatives, were subsequently analyzed by high performance liquid chromatography. This sampling technique and analytical method allows quantitative determination of 15 individual aldehydes.[5]

Diluted exhaust samples for detailed HC determination were collected in Tedlar* bags, and subsequently analyzed by gas chromatography. Three gas chromatographs equipped with flame ionization detectors (FIDs) were used for the analysis. A 2 meter × 2.2 mm OD Molecular Sieve 13X column was used for methane determination. A 5 meter × 2.2 mm ID stainless steel column packed with 60–80 mesh silica gel was used for C_2–C_3 HC determination, and a 125 meter × 0.5 mm ID 7.5% hydrophobic silica soft glass capillary column was used for C_4–C_{13} HC determination. The GC procedure for C_2–C_3 and C_4–C_{13} HC determination was originally developed for roadway sample analysis and used a cold trap injector for sample preconcentration.[6] In the present study, sample preconcentration was not necessary and the cold trap was replaced with a 10 cc stainless steel sample loop. The method provided quantitation for over 200 HC species.

Regulated emissions (THC, CO, NO_x) were sampled and analyzed using standard certification procedures.[7] THC emissions are reported as nonoxygenated HC by using a procedure to correct the THC value for FID response to MeOH.[8]

Exhaust emissions were determined for two driving cycles, the UDDS and a modified version of the UDDS. A time versus speed trace for the UDDS is given in Figure 2. The UDDS is the urban driving cycle of the federal test procedure (FTP). The FTP includes three test phases: a cold start transient phase, a stabilized phase, and a hot start transient phase. There is a 10-minute engine-off soak period between phases two and three. Emissions from each phase are analyzed separately and then combined using a weighting formula to produce a composite FTP emission rate. The modified version (MFTP) includes an additional initial five-minute warm up idle phase. The remaining three phases are identical to the FTP except that phase one is not cold started. Composite emission rates for the MFTP are calculated by combining idle phase emissions with the cold transient phase emissions and then applying the weighting formula as with the FTP.

Triplicate tests were conducted for both cycles at each test temperature. Baseline FTP and MFTP tests were conducted at 70°F. Low temperature tests were conducted at 40 and 20°F. Prior to each test, the Escort was soaked overnight in the TCTC at the next day's test temperature. TCTC, engine oil and coolant, and fuel temperatures were monitored prior to and during each test. The chassis dynamometer was thoroughly warmed up and calibrated immediately before each test. Dynamometer calibration was greatly simplified by locating its power absorption unit and load cell outside of the TCTC, so that their operation would not be adversely affected by the low test temperatures. Identical road load curves and inertia settings were used for all test temperatures.

Evaporative Emissions Determination

Vehicle evaporative emissions tests were conducted in a sealed housing for evaporative determinations (SHED). To determine evaporative emission rates, the vehicle was sealed within the SHED enclosure and tested in accordance with the FTP. At the conclusion

* Tedlar is a trade name of E.I. Dupont de Nemours & Co., Inc.

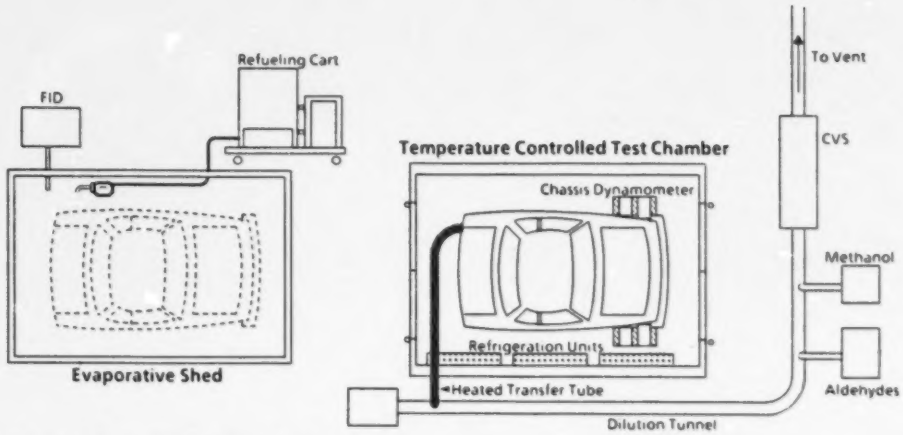

Figure 1. Overhead view of testing facility.

of each evaporative test, samples were taken from the SHED in a 60 L Tedlar bag for analysis of MeOH and detailed HC.

For MeOH determination, the contents of the 60 L sample bag were bubbled through water filled impingers to produce MeOH in an aqueous solution which was then analyzed by gas chromatography. A portion of the bag sample was retained for detailed HC analysis using the gas chromatography procedure of Black et al.[9] The method permitted quantitation of 83 different C_3–C_{11} HC.

Samples for THC analysis were taken directly from the SHED to an FID. As with exhaust emissions, evaporative THC are reported as non-oxygenated THC by correcting the THC value for FID response to MeOH.

Diurnal and hot soak evaporative emission tests were conducted in conjunction with the FTP, as shown in the flowchart in Figure 3. Following an overnight soak in the TCTC at the test temperature, the Escort was pushed into the SHED for the diurnal fuel tank heat build. During the diurnal test, tank fuel was elevated in temperature using ramps of 20 to 44°F for the 20°F tests, 40 to 64°F for the 40°F tests, and 60 to 84°F for the 70°F test. Following the diurnal test, the Escort was pushed back into the TCTC and allowed to equilibrate at the test temperature, usually requiring 2 or 3 hours. After temperature equilibrium, the UDDS was run, followed immediately by the hot soak evaporative test. The SHED was not equipped to be operated at reduced temperatures, and was, therefore, maintained at laboratory temperatures near 70°F. This had little effect on the diurnal tests which start with engine and fuel cold. The hot soak tests, however, begin with engine and fuel warm. If the SHED had the capability for reduced temperature operation, the engine and fuel would be more rapidly cooled, possibly reducing hot soak emissions.

Refueling Emissions Determination

Refueling experiments were conducted to determine the quantity and character of emissions to the environment during vehicle fueling. The experiments were conducted using a SHED procedure similar to that used in evaporative emission determination. The SHED was fitted with sealable sampling ports, thermocouples, an air mixing system, a gas-tight neoprene port surrounding the gasoline delivery hose and nozzle, and a large neoprene gas-tight glove which allowed manipulation of the delivery hose and nozzle by the operator from outside the SHED. The gasoline delivery hose was connected to the fuel cart which was maintained at 88°F.

The Escort's fuel tank was drained of all fuel prior to each refueling test and then filled with 2 gallons of test fuel. This simulated the initial (before refueling) fuel tank condition. The vehicle was then pushed into the shed and a heat blanket was fitted to the bottom exterior surface of the fuel tank to bring the tank fuel up to the desired test temperature of 78, 88, or 98°F by heating at a moderate rate. The SHED's interior temperature was likewise maintained at the desired test temperature of 78, 88, or 98°F by use of supplemental heat lamps located within the SHED. After the tank fuel had reached its proper temperature, a temperature differential of 2°F between the vapor in the tank and the liquid fuel was maintained for a minimum of 15 minutes. At this time the SHED was closed and sealed and background THC levels were measured using an FID corrected for MeOH response. Using the neoprene glove port, the SHED operator then uncapped the fuel tank and began filling the vehicle. Fuel flow was normally maintained at 8 gallons per minute through a standard OPW 11-A automatic unleaded gasoline dispensing nozzle. The Escort was fueled with 9.5 gallons of 88°F dispensed fuel

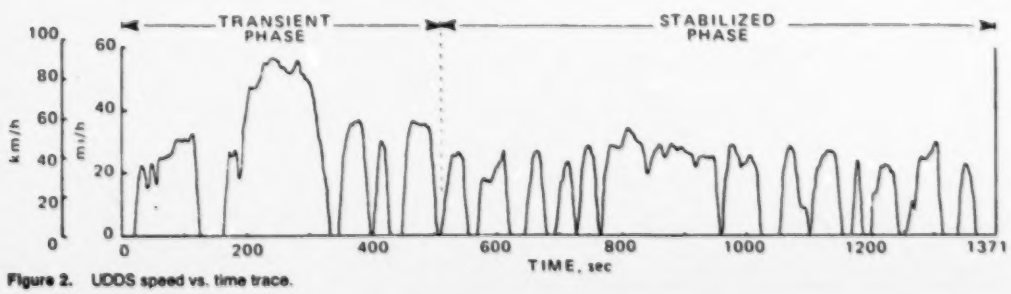

Figure 2. UDDS speed vs. time trace.

and the fuel tank recapped. The 9.5 gallons of dispensed fuel plus the 2 gallons that were initially in the tank accounted for over 95 percent of the Escort's 12 gallon fuel tank capacity.

THC levels in the SHED were continuously monitored with an FID to determine when the vapor had become thoroughly mixed with the SHED air. In normal practice, the THC levels stabilized about 15 minutes after replacement of the gas cap. At that time the FID was calibrated with known concentrations of propane in air, and a THC measurement was taken. In addition, a SHED sample was taken in a 60 l Tedlar bag for MeOH and detailed HC analysis using the same techniques that were used for evaporative emission determination. Temperature and pressure in the SHED and temperatures of the fuel cart, the delivered fuel (Td) and the vehicle's (Tt) fuel tank were recorded at the beginning and end of each test. The mass emission of THC from the refueling operation was calculated using procedures outlined in the SAE Recommended Practice for vehicle refueling emissions measurement.[10]

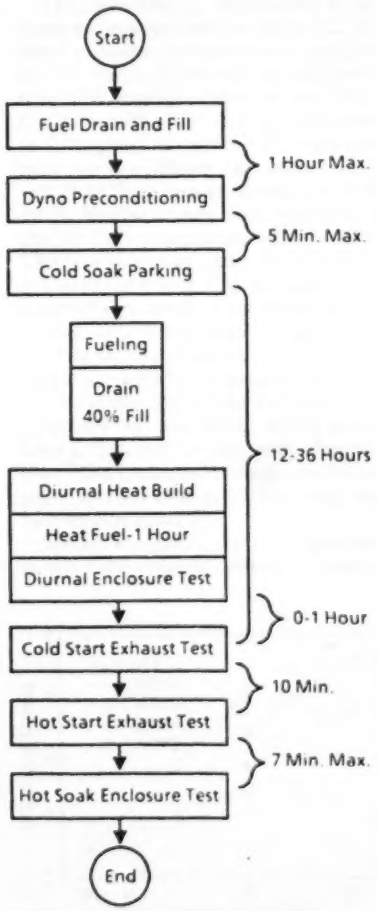

Figure 3. FTP evaporative and exhaust test sequence.

Selection of Refueling Parameters

The major parameters affecting refueling emissions include: 1) fuel volatility, customarily expressed as Reid vapor pressure (RVP); 2) dispensed fuel temperature (Td); 3) temperature of the fuel in the vehicle's tank prior to refueling, hereinafter referred to as tank temperature (Tt); 4) vehicle design configuration; and 5) the quantity of fuel dispensed. For this study, two fuels appropriate for summertime, the M85sg and the M100 fuels, were used because refueling (HC) emissions contribute to ozone violations which occur primarily during the summer months (May through September). A Td of 88°F was chosen because it represents the weighted average dispensed fuel temperature for the Southeastern United States during the previously mentioned summer months of May through September.[9]

Tt's of 78, 88, and 98°F were chosen to explore the relationship of refueling emissions with tank temperature. Because a major parameter in determining the magnitude of refueling emissions is the difference between the tank fuel temperature (Tt) and the dispensed fuel temperature (Td), three ΔT values, $^{-}10$, 0, and $^{+}10$°F, corresponding to the selected Tt levels of 78, 88, and 98°F, respectively, were selected for examination. A quantity representative of the typical "fill up," 9.5 gallons, (i.e. 95 percent of tank capacity), was dispensed to the tank during the experiments.

Results and Discussion

Exhaust Emissions

Baseline* CO emissions (7.0 g/mile) and THC emissions (0.49 g/mile) both exceeded the standard levels of 3.4 g/mile and 0.41 g/mile, while NO_x emissions (0.65 g/mile) were well below the 1.0 g/mile standard. These results suggest that the Escort was operating under fuel rich combustion conditions and/or catalyst efficiency had deteriorated. Because the vehicle had good driveability, no attempts were made to bring the emissions into compliance with the standard levels.

Sensitivity of exhaust emissions to operating temperature, cycle selection, and fuel composition is demonstrated in Figures 4–8. FTP and MFTP emissions are plotted as a function of test temperature. CO, MeOH, and THC emission patterns were similar. FTP CO and MeOH emissions at 40°F increased 400 percent over the baseline levels and at 20°F increased 700 percent over the baseline levels. THC emissions increased 227 percent at 40°F and 513 percent at 20°F. Similar CO and THC trends have been observed with gasoline fueled vehicles and are consistent with increased carburetion fuel enrichment at lower temperatures.

To differentiate between the influence of temperature and fuel type on emissions, 40°F tests were run with both M85sg and M85wg fuels. CO, MeOH, and THC emissions were all reduced when using the more volatile M85wg fuel. Fuel type comparisons were also made at 70°F, where both the M85sg and M100 fuels were used. CO and MeOH emissions showed little change when the Escort was fueled with the M100 fuel, while THC emissions, consisting mostly of methane, were significantly reduced.

Formaldehyde emissions (which accounted for more than 90 percent of the total aldehydes from this vehicle) were less temperature sensitive and more fuel sensitive than the HC, MeOH, and CO emissions. Emission rates ranging from about 0.29 to 0.33 g/mile were observed with the M85wg fuel and about 0.34 g/mile with the M100 fuel, while values ranging from about 0.12 to 0.20 g/mile were observed with the M85sg fuel.

NO_x emissions remained low and relatively constant for all test conditions. The 1.0 g/mile standard was exceeded only once, for the 40°F FTP on the M85sg fuel, when the emission rate was found to be 1.02 g/mile.

Typically, vehicle emissions are highest during the cold start transient phase of the FTP, where the vehicle is placed under load before the engine and catalytic converter have reached normal operating temperatures. At reduced test temperatures, cold start emissions are further increased due to decreased fuel vaporization. Counteracting these influences in the real world is a tendency for vehicle owners to "warm-up" (idle) their vehicles for a longer period of time during cold weather. The effect of vehicle warm-up time on emissions was examined by running a second series of low temperature tests (MFTPs) which increased the normal FTP warm-up time from 20 seconds to 320 seconds. Results of the MFTP tests are plotted in Figures 4–8. CO, MeOH, and THC emissions were reduced by the additional warm-up time. Formaldehyde emissions were generally increased by the preliminary idle period, while NO_x emissions showed little change.

Table II provides comparison of FTP tailpipe HC compositions. Results for the MFTP, although not shown, are similar to those with the FTP. Significant shifts in the HC emissions composition occur with M85sg fuel on increasing the temperature from 40 to

* FTP emissions determined under test conditions similar to those of certification emissions testing (i.e. test temperature = 70°F and test fuel = M85sg)

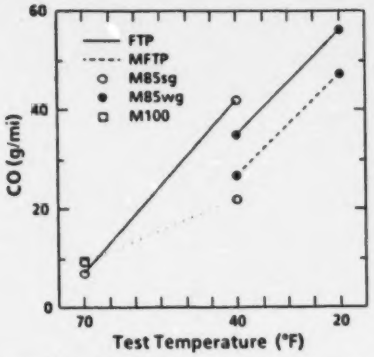

Figure 4. CO emission rates vs. test temperature.

70°F. As the temperature increased, the THC emission rate decreased and the paraffin fraction increased due primarily to the refractory nature of methane. Methane is not as effectively reduced by the catalyst as the other HC.

Evaporative Emissions

THC and MeOH evaporative emissions are summarized in Table III. Diurnal emission patterns were sensitive to fuel composition and test temperature. THC emission rates for the M85sg fuel were 3.38 g/test at 70°F compared to 2.14 g/test at 40°F. THC emission rates for the M85wg fuel were 4.61 g/test at 40°F compared to 0.43 g/test at 20°F. Similar trends were observed in the M85wg hot soak tests with the 40°F THC emissions at 1.25 g and the 20°F emissions at 0.56 g. The hot soak THC emissions, however, were higher in the M85sg 40°F tests than in the M85sg 70°F tests. As previously discussed, the evaporative SHED temperature could not be controlled at the reduced temperatures 40 and 20°F, which could have influenced the hot soak observation. THC evaporative emissions (diurnal + hot soak) were highest with the M85wg fuel at 40°F.

MeOH accounted for 12–22 percent of the total organic diurnal emissions with the M85 fuels, and the emission levels decreased with decreasing test temperature. MeOH accounted for 37–81 percent of the total organic emissions for the hot soak, and as with the diurnal tests, the hot soak methanol emissions decreased with decreasing test temperature. Total (diurnal + hot soak) MeOH emissions were highest with the M85sg blend at 70°F.

Diurnal and hot soak MeOH emission rates with the M100 test fuel @ 70°F were about half of that found with the M85sg blend. Selected diurnal vapor compositions are given in Table IV, and hot soak vapor compositions in Table V. The evaporative HC emissions are dominated by paraffins with n-butane and isopentane most prevalent.

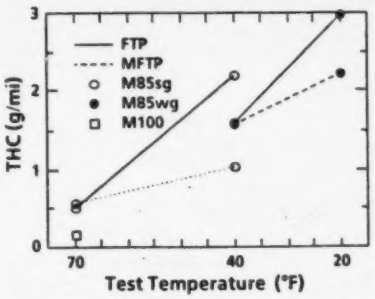

Figure 6. THC emission rates vs. test temperature.

Refueling Emissions

Refueling emission rates in grams per gallon are listed as a function of tank temperature and fuel type in Table VI. An interesting aspect of the M85 and M100 refueling tests was that the MeOH emission rates were virtually identical at all three test temperatures with both fuels, averaging 0.74 ± .05 g/gal of MeOH for all conditions.

It should be noted that the M100 THC emission rates given in Table VI resulted from fuel delivery system "memory" effects, that is, HC contamination from previous refueling tests using theM85sg fuel. While repeated flushing and purging of the fuel cart and associated plumbing resulted in a steadily decreasing THC emissions fraction, a small THC portion persisted for the duration of the refueling study. Because a fuel analysis of the M100 fuel indicated no HC contamination, the THC emissions portion should predictably disappear given sufficient time for fuel delivery system flushing. No fuel HC contamination was detected in the exhaust and diurnal/hot soak evaporative tests, where a different fuel delivery system was used.

With the M85 fuel, as the temperature of the tank fuel was increased from 78 to 98°F (delivery fuel kept at a constant 88°F), the total refueling emission rate decreased from 3.35 to 2.88 g/

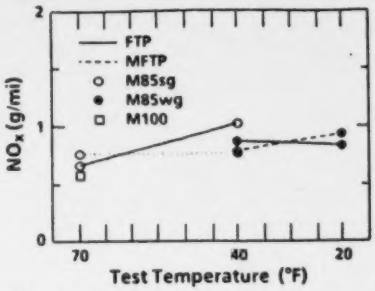

Figure 7. NO_x emission rates vs. test temperature.

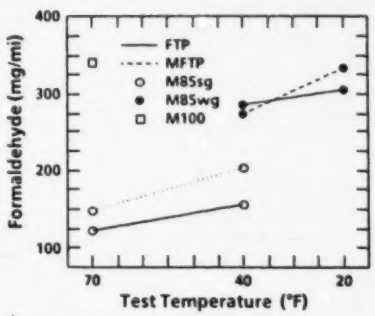

Figure 8. Formaldehyde emission rates vs. test temperature.

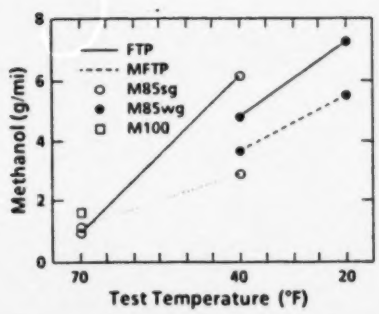

Figure 5. Methanol emission rates vs. test temperature.

Table II. Exhaust HC compositions.

Compound	M85sg 70°F % of Total	M85sg 40°F % of Total	M85wg 40°F % of Total	M85wg 20°F % of Total	M100 70°F % of Total
Paraffins	67.8	44.9	42.9	45.6	86.8
Olefins	12.2	18.8	15.0	13.9	10.3
Aromatics	17.5	32.3	40.2	38.1	2.2
Methane	33.8	12.3	14.5	16.3	83.1
Ethylene	5.1	7.6	7.3	5.8	7.6
Acetylene	1.1	1.5	0.7	0.9	0.6
N-Butane	6.5	2.2	3.3	4.1	1.0
Isopentane	5.4	3.4	4.3	5.2	0.0
Benzene	2.3	3.3	4.9	5.4	1.1
Toluene	6.5	10.8	20.3	20.0	1.1

gal. The HC portion of the refueling emission rate averaged 77 percent of the total, ranging from 2.63 g/gal at 78°F to 2.15 g/gal at 98°F. Agreeing with observations from previous studies with hydrocarbon fuels, the M85sg HC emissions were temperature dependent.[9,11] MeOH emissions, however, were invariant with temperature, averaging 0.73 g/gal for all test temperatures.

Detailed HC analysis of the 78 and 98°F refueling HC vapors are listed in Table VII, including C_3–C_{11} carbon number distribution, average carbon number, and the highest eight vapor components. Table VII indicates an increase in average carbon number, from 5.08 at 78°F to 5.24 at 98°F, suggesting a more significant contribution of the lower volatile, higher molecular weight components of the fuel at the higher tank temperature. The HC refueling vapor was comprised of 82.3 percent paraffins, 13.6 percent olefins, and 3.0 percent aromatics; the gasoline (liquid) portion of the fuel was comprised of 52.2 percent paraffins, 10.2 percent olefins, 37.6 percent aromatics, with an averge carbon number of 7.22. Table VII also indicates that the butanes and pentanes comprise about 75 percent of the total HC refueling vapor.

Aggregate Organic Emissions

Aggregate organic emissions (sum of tailpipe, evaporative, and refueling emissions) for the Escort are presented in Table VIII.

To determine aggregate emissions, diurnal (Di) and hot soak (Hs) evaporative emissions from Table III are combined into an evaporative equivalent emission rate (g/mile), based on the assumption that the average vehicle makes 3.05 trips/day and the daily average distance travelled is 31.3 mile/day. Refueling emissions (Re), expressed in g/gal are divided by the average fuel economy (FE), to obtain refueling emissions expressed as g/mile. Aggregate emissions shown for the Escort are for a summer scenario (70°F) using M85sg fuel.

For comparison, emission characteristics are also given for a typical gasoline fueled vehicle (shown in parenthesis in Table VIII), assuming identical tailpipe, evaporative, and refueling organic emission rates for the Escort and gasoline fueled vehicle. Tailpipe emission rates were calculated for the gasoline vehicle based on known percentages of each organic group typically found in auto exhaust.[12]

Of note is the change in organic mix emitted from the Escort relative to typical gasoline vehicles. The Escort has a relatively low non-methane HC fraction compared to gasoline vehicles. Because non-methane HCs play an important role in the formation of ozone in the atmosphere, their reduction would be beneficial to air quality. Of concern, however, is the increased fraction of formaldehyde emitted from the Escort. Formaldehyde is more photochemically reactive than non-methane HCs and therefore could seriously erode the benefits derived from a reduction in the non-methane HCs.

Table III. Diurnal and hot soak evaporative emissions.

		Diurnal		Hot Soak	
Fuel Type	Test Temp. F	THC g	Methanol g	THC g	Methanol g
M85sg	70	3.38	0.95	0.59	2.66
M85sg	40	2.14	0.54	0.76	1.55
M85wg	40	4.61	0.61	1.25	0.75
M85wg	20	0.43	0.10	0.56	0.58
M100	70	*	0.48	*	1.06

* Below quantitative limits of 0.01 g.

Table IV. Diurnal HC vapor composition.

Component	M85sg 70°F % of Total	M85sg 40°F % of Total	M85wg 40°F % of Total	M85wg 20°F % of Total
Paraffins	83.5	81.4	83.0	72.5
Olefins	12.6	13.8	13.5	14.4
Aromatics	3.0	3.7	2.8	11.5
Iso-Butane	5.0	5.0	16.0	12.3
N-Butane	37.3	36.9	33.4	25.4
Isopentane	21.7	21.7	21.3	16.9
N-Pentane	3.7	2.7	3.4	3.2

Table V. Hot soak HC vapor composition.

Component	M85sg 70°F % of Total	M85sg 40°F % of Total	M85wg 40°F % of Total	M85wg 20°F % of Total
Paraffins	71.7	74.6	73.3	63.8
Olefins	16.3	13.5	14.8	14.6
Aromatics	9.7	9.9	10.3	19.9
Iso-Butane	1.9	2.8	12.2	7.6
N-Butane	17.3	24.8	27.6	19.9
Isopentane	18.3	20.2	18.7	17.4
N-Pentane	3.8	3.7	2.2	2.6

Table VI. Methanol, hydrocarbon, and total refueling emissions as a function of fuel type and tank temperature.

Fuel type	Tank temp,°F	ΔT °F	Methanol g/gal	THC g/gal	Total refueling emissions, g/gal
M85sg	78	−10	0.72	2.63	3.35
(Td=88°F)	88	0	0.73	2.52	3.25
	98	+10	0.73	2.15	2.88
M100	78	−10	0.80	0.27	1.06
(Td=88°F)	88	0	0.79	0.11	0.89
	98	+10	0.66	0.11	0.77

Conclusions

- UDDS exhaust CO and MeOH emission rates showed similar increases as test temperature was reduced. Exhaust THC emission rates were also elevated at the lower test temperatures, but to a lesser degree than CO and MeOH. Exhaust NO_x emission rates indicated

Table VII. M85sg HC refueling vapor composition at 78°F and 98°F temperature conditions.

Carbon number	78°F Tests	98°F Tests
	Carbon number distribution percentages	
C_3	0.64	0.00
C_4	41.56	38.20
C_5	32.75	33.73
C_6	10.03	10.67
C_7	5.48	4.64
C_8	8.76	9.40
C_9	0.44	1.38
C_{10}	0.34	1.76
C_{11}	0.00	0.00
Average carbon number	5.08	5.24
	Highest 8 vapor components	
Component	78°F Tests % of Total	98°F Tests % of Total
Isobutane	4.38	3.63
N-Butane	34.03	31.99
Isopentane	22.78	22.97
N-Pentane	3.93	4.28
2,3-Dimethylbutane	1.97	2.12
2-Methylpentane	2.50	2.70
3-Methylpentane	1.58	1.82
2,2,4-Trimethylpentane	3.60	3.55

Table VIII. Aggregate organic emissions for Escort and typical gasoline vehicle.

Compound	Tailpipe g/mile	Evaporative[1] g/mile	Refueling[2] g/mile	Aggregate g/mile
Formaldehyde	0.12 (0.01)[3]	0.00 (0.00)	0.00 (0.00)	0.12 (0.01)
Methanol	0.96 (0.00)	0.31 (0.00)	0.05 (0.00)	1.32 (0.00)
Non-methane HC	0.33 (1.35)	0.17 (0.48)	0.15 (0.20)	0.65 (2.03)
Methane	0.16 (0.21)	0.00 (0.00)	0.00 (0.00)	0.16 (0.21)
Total	1.57 (1.57)	0.48 (0.48)	0.20 (0.20)	2.25 (2.25)

[1] Evaporative, g/mile = $\frac{\text{Di,g/day} + (3.05\ \text{trip/day} * \text{Hs,g/trip})}{31.3\ \text{mile/day}}$

[2] Refueling, g/mile = $\frac{\text{Re, g/gal}}{\text{FE, mile/gal}}$

[3] Emission rates for gasoline vehicle are given in parenthesis.

little sensitivity to test temperatures.

- UDDS exhaust formaldehyde emission rates indicated a greater fuel type dependence than did THC, CO, and MeOH. Formaldehyde emission rates were highest with the M100 and M85wg fuels at about 0.3 g/mile.
- Low temperature (40 and 20°F) CO, MeOH, and THC emissions were significantly lower with the modified UDDS (which included a 5-minute initial warm-up idle) than with the standard UDDS. The warm-up idle, however, had little impact on NO_x emission levels. Formaldehyde emission rates were generally elevated with the modified UDDS.
- MeOH accounted for only 12–22 percent of the total organic diurnal evaporative emissions, and 37–81 percent of the total organic hot soak evaporative emissions. MeOH evaporative emissions decreased as the test temperature decreased.
- Diurnal THC evaporative emissions were sensitive to both test temperature and fuel type. For a given fuel, emission rates decreased as test temperatures decreased. Highest THC emissions were found for the 40°F tests using the M85wg fuel.
- MeOH refueling emissions were invariant with changes to both fuel tank temperatures and fuel type. THC emissions decreased with increasing tank temperature. The THC portion of the refueling emission averaged 77 percent of the total organic refueling emission with M85sg fuel.
- Formaldehyde accounted for 5.3 percent; MeOH, 58.7 percent; and non-methane HC, 28.9 percent of the aggregate organic emissions from the Escort under summer ambient conditions.

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